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40. Stoichiometric Number and Universal Kinetic Law in the Neighbourhood of Equilibrium. I

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The present author has previously introduced the stoichiometric number¹⁾²⁾ as a characteristic to the mechanism of a reaction, consisting in general of several elementary reactions. Below will be pointed out some of its properties and derived a kinetic law valid universally in the neighbourhood of equilibrium with special reference to that of the rate-determining step.

I

The stoichiometric number of a constituent elementary reaction is defined²⁾ as the ratio of number s of its occurrence over that p of the simultaneous completion of the overall reaction *i.e.* s/p . It is hence in general the ratio of two positive integers or a positive rational number, but not necessarily an integer itself as it might seem at first sight. Neither it is characteristic of the relevant elementary reaction and the overall reaction alone, but depends on the course of the reaction or on the sequence of the elementary reactions.

These points will be illustrated below.

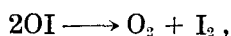
Assume the homogeneous thermal decomposition of nitrous oxide,



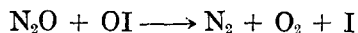
catalyzed by iodine atom I at equilibrium with molecule I_2 , as usual to begin with the step



Its stoichiometric number is now 2 or 1 according as it is followed by



or by



to complete the overall reaction, since half or whole the left-hand member $2\text{N}_2\text{O}$ of (1) is brought down every step (2) in the respective case.

In the extreme case of the steady chain reaction, the reciprocal of the chain length corresponds directly to the stoichiometric number of the chain initiating step. The quantum yield of a steady photochemical reaction is thus reciprocal of the stoichiometric number of the initiating photochemical one, which obeys itself the Einstein's law.

II

The present author has previously derived¹⁾²⁾ on the basis of $h\nu_s$

statistical mechanical theory of the reaction rate³⁾⁴⁾, the relations

$$V_s = \vec{\mathfrak{K}} \left\{ 1 - \exp \left(- \frac{\Delta\mu}{\nu(r)RT} \right) \right\}, \quad \vec{\mathfrak{K}} / \overleftarrow{\mathfrak{K}} = \exp \left(- \frac{\Delta\mu}{\nu(r)RT} \right) \quad (3. V), (3. \mathfrak{K})$$

between the stoichiometric number $\nu(r)$ of the rate-determining step, the steady rate V_s of the overall reaction, the free energy increase $\Delta\mu$ associated with it, its forward one-direction rate $\vec{\mathfrak{K}}$ and backward one $\overleftarrow{\mathfrak{K}}$, assuming all other steps practically at equilibrium.

Let now,

$$\delta^L = \delta^R \quad (4. \delta)$$

represent the overall reaction, where

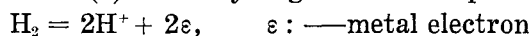
$$\delta^L = \sum_i \nu_i^L \delta_i^L, \quad \delta^R = \sum_r \nu_r^R \delta_r^R \quad (4. L), (4. R)$$

δ_i^L etc. or ν_i^L etc. being respectively molecular formulas or appropriate coefficients on the left-hand side of (4. δ), and δ_r^R etc. or ν_r^R etc. those on the right. The $\Delta\mu$ is now expressed in terms of the chemical potentials $\mu^{\delta_i^L}$ etc. respectively of δ_i^L etc., as

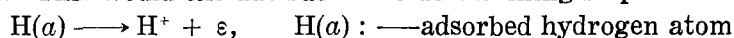
$$\Delta\mu = \sum_r \nu_r^R \mu^{\delta_r^R} - \sum_i \nu_i^L \mu^{\delta_i^L}. \quad (5)$$

Eq. (3. V) and (3. \mathfrak{K}) holds as it follows from its derivation, whenever the above premises on the rate-determining step is valid, irrespective of the underlying mechanism or of the type of the reaction, homogeneous or heterogeneous.

Using (3. V) directly, Horiuti and Ikusima¹⁾ have previously determined $\nu(r)$ of the hydrogen electrode process on platinum,



at 1. This would exclude such rate-determining step as

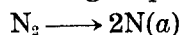


whose $\nu(r)$ is 2, if preceded by the step, $\text{H}_2 \rightarrow 2\text{H}(a)$, but Frumkin²⁾ have reported later with the same case that $\nu(r)=2$. The situation is yet to be settled.

Enomoto and Horiuti³⁾ have recently determined $\nu(r)$ of the catalyzed ammonia synthesis reaction



at ordinary pressure around 430°C at 2. This conclusion rules out the generally accepted rate-determining step



of which $\nu(r)=1$, if (6) follows the sequence, $\text{N}_2 \rightarrow 2\text{N}(a)$, $\text{H}_2 \rightarrow 2\text{H}(a)$, $\text{N}(a) + \text{H}(a) \rightarrow \text{NH}(a)$, $\text{NH}(a) + \text{H}(a) \rightarrow \text{NH}_2(a)$, $\text{NH}_2(a) + \text{H}(a) \rightarrow \text{NH}_3$, where (a) denotes adsorbed atom or atom group.

III

Eq. (3. V) gives directly the relation of V_s being proportional to $\Delta\mu$,

$$V_s = - \frac{\vec{\mathfrak{R}}_e}{\nu(r)RT} \Delta\mu$$

in the neighbourhood of equilibrium by expanding its right-hand side with respect to $\Delta\mu/\nu(r)RT$ and neglecting terms of higher than the first order, where $\vec{\mathfrak{R}}_e$ is the one-direction rate at equilibrium. The proportionality factor $\vec{\mathfrak{R}}_e/\nu(r)RT$ is finite and different from zero according to the definition of the quantities involved.

The similar relation has been put forward by Prigogine, Outer, and Herbo⁷⁾ and by Manes, Hofer, and Weller⁸⁾ on the basis of the thermodynamical fact that V_s and $\Delta\mu$ vanish simultaneously at equilibrium. This assures that the zeroth order term of the expansion vanishes but not that the first order one does not, which is essential for the above statement of proportionality. Otherwise V_s should be called proportional to $\Delta\mu^n$, where $n(>1)$ is the order of the first non-vanishing term of the expansion.

The proportional relation of V_s to $\Delta\mu$ has been derived by Gilkerson, Jones, and Gallup⁹⁾ according to the theory of absolute reaction rate due to Eyring et al.¹⁰⁾ The equation arrived at by the latter authors corresponds to the special case of the above one when $\nu(r)=1$, or more closely when the reaction consists in a single step.

IV

Below will be derived from (3. V) a kinetic law valid universally in the neighbourhood of equilibrium and simultaneously a general formula giving $\nu(r)$ in terms of directly observable quantities.

The system treated here is a closed one, in which reaction (4. δ) with the rate-determining step is going on at constant temperature and at constant volume or pressure, being solely responsible for inter-conversion of chemical species δ_i^L etc., so that the momentary number $n^{\delta_i^L}$ etc. of them existing in the system are respectively uniquely defined by a single variable m according to the relation

$$\begin{aligned} m - m_e &= \frac{n_e^{\delta_1^L} - n^{\delta_1^L}}{\nu_1^L} = \dots = \frac{n_e^{\delta_i^L} - n^{\delta_i^L}}{\nu_i^L} = \dots \\ &= \frac{n_e^{\delta_1^R} - n^{\delta_1^R}}{\nu_1^R} = \dots = \frac{n_e^{\delta_r^R} - n^{\delta_r^R}}{\nu_r^R} = \dots \end{aligned} \quad (7)$$

suffix e denoting the particular value at equilibrium^{*)}.

Defining now activity a^δ of respective chemical species δ , which stands for δ_i^L 's and δ_r^R 's, as

$$RT \log a^\delta = \mu^\delta \quad (8)$$

*) The origin of m is quite arbitrary: It may well be taken at the initial state \geq here $n^{\delta_i^L} = n_0^{\delta_i^L}$ etc. or at equilibrium, suffix 0 denoting the value at time $t=0$. In the latter case, m_e is of course zero.

(3. V) and (3. \mathfrak{R}) may respectively be written in the form

$$V_s = \vec{\mathfrak{K}} \left\{ 1 - (a^{\delta^R}/a^{\delta^L})^{1/\nu(r)} \right\}, \quad \vec{\mathfrak{R}}/\vec{\mathfrak{K}} = (a^{\delta^L}/a^{\delta^R})^{1/\nu(r)} \quad (9. V), (9. \mathfrak{R})$$

where

$$a^{\delta^L} = I^L (a^{\delta_i^L})^{\nu_i^L}, \quad a^{\delta^R} = I^R (a^{\delta_r^R})^{\nu_r^R}. \quad (9. L), (9. R)$$

It follows from the definition that $a^{\delta_i^L}$ etc. are respectively functions solely of m and that

$$a^{\delta^L} = a^{\delta^R} \quad \text{at} \quad m = m_e. \quad (10)$$

Expanding now the right of (9. V) with respect to m around the equilibrium point m_e and neglecting terms higher than the first order, we have

$$V_s = - [\mathfrak{K}] (m - m_e) \quad (11. m)$$

where

$$[\mathfrak{K}] = \vec{\mathfrak{K}}_e a_{m/\nu}(r), \quad a_m = \left\{ \frac{d}{dm} \log (a^{\delta^R}/a^{\delta^L}) \right\}_e \quad (11. \mathfrak{K}), (11. a)$$

zeroth order term vanishing according to (9. V) and (10).

The increment of m defined by (7) corresponds to the number of conversion of δ^L of (4. δ) into δ^R . Expressing V_s by the increasing rate of m with time t , as

$$V_s = dm/dt \quad (12. V)$$

we have, according to (11. m),

$$dm/dt = - [\mathfrak{K}] (m - m_e) \quad (12. D)$$

or by integration,

$$\log |m - m_e| = - [\mathfrak{K}] t + \text{constant}. \quad (12. I)$$

The "monomolecular law" (12. D) or (12. I) would be useful for reasonably locating equilibrium without waiting it for "infinite" time, while $[\mathfrak{K}]$ necessarily brought about by the procedure of the location, incorporated with $\vec{\mathfrak{K}}_e$ and a_m , determines $\nu(r)$, affording a criterion for the mechanism as exemplified above.

The quantity a_m will be developed for its experimental determination with a few particular cases in the subsequent paper.

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